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QUARTERLY TECHNICAL REPORT

on

PREPARATION OF FLUORINE CONTAINING COMPOUNDS

at

THE UNIVERSITY OF FLORIDA

under

CONTRACT Nonr-580(03); NR 356-333

PERIOD COVERED

February 1, 1956 to April 30, 1956

by

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R. D. Dresdner
J. A. Wethington, Jr.
J. A. Young

ANNUAL SUMMARY

SUMMARY OF ELECTROCHEMICAL SYNTHESSES IN HYDROGEN FLUORIDE

Large Scale Operations

These operations were performed in electrochemical equipment nominally designed to use electrical conditions of from 50 to 100 amperes at between 4.8 to 6.0 volts D.C. The experimentally imposed conditions of operation are dependent upon a number of variables the most important of which are (1) the nature of the electrolyte, (2) the nature of the products, (3) the operating temperatures and (4) the concentration of the electrolyte.

The following table offers a summary of the results of the electrochemical operations performed in the last year.

| <u>Starting Material</u> | <u>Amount (gr)</u> | <u>H₂ Gas Evolved in Liters</u> | <u>Products or B.P. Range in °C.</u> | <u>Amount of Each Isolated in Grs.</u> |
|---|--------------------|--|---|--|
| C ₄ H ₉ COCl | 1320 | 2980 | Below -78° -6 to -8° C ₄ F ₁₀ 8 to 29 CF ₂ -CF ₂ CF ₂ -CF ₂ C ₄ F ₉ COF Other acid fluorides | Not recorded 25 70 25 175 100 35 |
| (CH ₂) ₄ (COCl) ₂ | 1857 | 2118 | Below -78° To 25° Unidentified esters esters { H(CF ₂) ₄ COOC ₂ H ₅ (CF ₂) ₄ (COOC ₂ H ₅) ₂ | Not recorded 268 120 75 80 |
| (C ₂ H ₅) ₂ O | 891 | 2700 | Cleavage Prods. (C ₂ F ₅) ₂ O Other fluorocarbon material | Not recorded 433 194 |

| <u>Starting Material</u> | <u>Amount (gr)</u> | <u>H₂ Gas Evolved in Liters</u> | <u>Products or B.P. Range in °C.</u> | <u>Amount of Each Isolated in Grs.</u> |
|---------------------------------------|--------------------|--|--------------------------------------|--|
| (CH ₃) ₂ NCOC1 | 1423 | 2998 | Liq. Air Condensate | 1750 |
| I. High initial conc. | | | (CF ₃) ₂ NCOF | 154 |
| (CH ₃) ₂ NCOC1 | 2175 | 4355 | Liq. Air Condensate | 2105 |
| II. Low initial conc. | | | (CF ₃) ₂ NCOF | 965 |
| (CH ₃) ₂ NCOC1 | | | Others | 350 |
| III. | 1930 | 4007 | (CF ₃) ₂ NCOF | 776 |

Small Scale Operations (800 cc. liquid capacity)

These operations are carried out in equipment which in most respects are prototypes of the large scale equipment but which have a nominal capacity of only 20 amperes and frequently in reality less than 20 amperes. Such operations are used to test new starting materials or to prepare small quantities of fluorine-containing substances to evaluate possible chemical reactions.

The following small scale operations have been made in the last year.

| <u>Starting Material</u> | <u>Amount (gr)</u> | <u>Products Isolated or B.P. Range</u> | <u>Amount of Each in Grams</u> |
|---|--------------------|--|--------------------------------|
| CF ₃ CON(CH ₃) ₂ | 569 | CF ₃ COF | 65 |
| | | (CF ₃) ₂ NCOF | 137 |
| | | CF ₃ CON(CF ₃) ₂ | 48 |
| | | Others | 129 |
| (CH ₃) ₂ NSO ₂ Cl | 157 | SOF ₂ SO ₂ F ₂ | 21 |
| | | Others | 21 |

| <u>Starting Material</u> | <u>Amount (gr)</u> | <u>Products Isolated or B.P. Range</u> | <u>Amount of Each in Grams</u> |
|--------------------------|--------------------|--|--------------------------------|
| $(C_2H_5)_2NCOCl$ | 595 | $(CF_3)_2NCOF$ | 73 |
| | | $CF_2CF_2OCF_2NC_2F_5$ | 365 |
| | | Mixture to 200°C. | 220 |
| | | Others | 73 |
| $(CH_3)_2NCON(CH_3)_2$ | 196 | CF_3NCOF | 110 |
| | | $(CF_3)_2NCON(CF_3)_2$ (?) | 10 |
| | | Others | 27 |
| $CH_3CON(CH_3)_2$ | 403 | No identifiable products 6-71°C. | 106 |
| $CH_3CH(OCH_3)_2$ | 250 | Below -70°C. | 62 |
| | | -56 to +40 (No flats) Tars in cell. | 35 |
| $O(CH_2CH_2)_2NCOF$ | 604 | $(CF_3)_2NCOF$ | 35 |
| | | $O(CF_2CF_2)_2NCOF$ | c. 30 |
| | | Unidentified, 0-240° | c. 300 |

ANNUAL SUMMARY OF OTHER WORK

1. Chemistry of $CF_3N=CF_2$

This compound can be made in nearly quantitative yield by pyrolysis of $(CF_3)_2NCOF$ in a nickel tube at 575°C. The precursor can be made by the electrochemical process as noted below.

The azomethine does not react with CF_3I , CF_3CN , or CF_2Br_2 when heated up to temperatures of 300-350°C in sealed glass tubes. It does react with CF_3SF_5 to give $(CF_3)_3N$. When heated alone or with the first three compounds, it forms an apparently polymeric material which is soluble in concentrated acids but very stable to heat and aqueous alkali. $CF_3N=CF_2$ forms a solid addition

compound with BF_3 at low temperatures.

Electrochemical reaction of aliphatic nitrogen compounds

Apparently, any compound having the structure $\text{R}_1\text{R}_2\text{N}-\text{C}-\text{M}$, where M is alkyl, amine or halogen and R is any alkyl group, will give $(\text{CF}_3)_2\text{NCOF}$ as one product, usually the predominant one. The bis-trifluoromethyl carbamyl fluoride has been identified in the products from $(\text{CH}_3)_2\text{NCOCl}$, $(\text{C}_2\text{H}_5)_2\text{NCOCl}$, $(\text{CH}_3)_2\text{NCON}(\text{CH}_3)_2$, $\text{CH}_3\text{CON}(\text{CH}_3)_2$, $\text{CF}_3\text{CON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{NCH}_2\text{CON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{NCH}_2\text{COOCH}_3$ and $\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCOCl}$.

Higher bis-alkyl carbamyl chlorides also give perfluoro heterocyclics, such as $\text{CF}_2\text{OCF}_2\text{CF}_2\text{NC}_2\text{F}_5$ from $(\text{C}_2\text{H}_5)_2\text{NCOCl}$.

Although the acid chlorides are preferred starting materials, other derivatives can sometimes be used. Thus, $\text{CF}_3\text{CON}(\text{CH}_3)_2$ and possibly $(\text{CH}_3)_2\text{NCON}(\text{CH}_3)_2$ gave some of the perfluoro analogue, while $(\text{CH}_3)_2\text{NCH}_2\text{COOCH}_3$ and $(\text{CH}_3)_2\text{NCH}_2\text{CON}(\text{CH}_3)_2$ gave $(\text{CF}_3)_2\text{NCF}_2\text{COF}$. Incorporation of a perfluoro group in the starting material may improve resistance toward fragmentation, as $\text{CF}_3\text{CON}(\text{CH}_3)_2$ gave the fluoro carbon analogue $\text{CF}_3\text{CON}(\text{CF}_3)_2$, while $\text{CH}_3\text{CON}(\text{CH}_3)_2$ did not.

It is possible by this method to make compounds as complex as $\text{O}(\text{CF}_2\text{CF}_2)_2\text{NCOF}$, although the yields are quite low.

2. When CF_3SF_5 was reacted with $\text{CF}_3\text{N}=\text{CF}_2$ at 520°C the major product was $(\text{CF}_3)_3\text{N}$ BP -10.9°C mw 220-222. MP $-114.7 \pm 0.5^\circ\text{C}$ and VP curve expressed by the equation $\text{Log } P_{\text{mm}} = \frac{1250}{T^\circ\text{K}} + 7.61$ between -80 and -10°C . The N_2 analysis was 6.36% (Calc.

THE MELTING POINT OF NEO-C₄F₁₂

Sir:

In a recent publication¹ the preparation and detection of neo-C₄F₁₂ in a mixture of C₄F₁₂ isomers was reported. The detection of the neo-C₄F₁₂ was made with the aid of nuclear magnetic resonance analysis (NMR). When the mixture of C₄F₁₂ isomers was removed from the sample tube in which the analysis was performed, it was noted that near the very end of the transfer some solid crystals remained in the tube. The crystals were sealed off in the tube and a melting point was determined. The melting range was observed to be 72-76°. When another aliquot of the mixture of C₄F₁₂ isomers was similarly treated, the crystalline residue was dissolved in pure CCl₄ and subjected to NMR analysis. The strong, single-peaked pattern obtained was interpreted as that which was characteristic of purified neo-C₄F₁₂.

More recently a larger sample of a mixture of C₄F₁₂ isomers was prepared in this laboratory. The mixture had a b.p. of 28.5-29.5° and a mol. wt. of 287-288 and was prepared from the reaction between (CF₃)₂SiF₄ and CF₃CF=CF₂ at 520°. Neo-C₄F₁₂ enrichment was achieved by evaporation *in vacuo* at temperatures below 0°. Finally, a sample of material highly enriched in neo-C₄F₁₂ was isolated. This residual material was a crystalline solid, reminiscent of CO₂, and it exerted a vapor pressure of 650 ± 2 mm at 26°. The solid sample amounted to one gram.

Aliquots of the sample were successively transferred *in vacuo* to heavy wall glass melting point tubes 2 mm. in diameter and 4 cm. long. These aliquots amounted to about 0.2 g. each and were sealed off, air-free, in their respective tubes. The

melting points of the five aliquots were determined in a water-bath with a thermometer and a stirrer. The temperature gradient over the depth of the bath did not exceed 0.2° and the rate of change of the temperature in the bath during the determinations did not exceed 0.25°/min. and was maintained at 0.1°/min. near and at the melting points. The following short table shows the melting range of the five successively condensed aliquots.

| Aliquot Order | Melting range in °C. |
|---------------|----------------------|
| 1 | 72.0-75.8 |
| 2 | 73.3-76.1 |
| 3 | 75.3-77.6 |
| 4 | 76.4-78.3 |
| 5 | 76.3-78.2 |

Accordingly, with the highest purity that could be obtained by the procedure outlined, the m.p. of neo-C₄F₁₂, under its own vapor pressure, was at least 78.3°.

Grateful acknowledgment is offered to Pvts. N. Muller and George Svatos for performing the NMR analyses, which were done at the Army Chemical Center, Md. Appreciation is expressed to Drs. F. W. Hoffman and T. C. Simmons of the Chemical and Radiological Laboratories of A.C.C. for making the NMR analyses possible. The work in this laboratory was supported by the Chemistry Branch of the Office of Naval Research under contract Nonr 580(03); 356-333.²

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(1) Richard Dresdner, *THIS JOURNAL*, 77, 6633 (1955).

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The Pyrolysis of Trifluoromethyl Sulfur Pentafluoride and its Reaction with Perfluoropropylene

BY RICHARD DRESDNER

RECEIVED SEPTEMBER 6, 1955

The pyrolysis of CF_3SF_5 , trifluoromethyl sulfur pentafluoride, and its reaction with C_3F_8 , perfluoropropylene, have been investigated. The experiments were carried out at temperatures between 425 and 518°. The only products found when CF_3SF_5 was heated, under the conditions outlined, were C_3F_8 , perfluoroethane, and SF_4 , sulfur tetrafluoride. When CF_3SF_5 and C_3F_8 were heated together at elevated temperatures, a series of fluorocarbons was isolated and identified.

Experimental

Apparatus.—The experiments were carried out in a closed system at approximately atmospheric pressure. The gases to be pyrolyzed or reacted were condensed air-free into a valved 1600-cc. stainless steel container. They were allowed to come to equilibrium at room temperature. The flow rate of the gases through the system was observed by their passage through a small bubbler containing a few cc. of dibutyl phthalate. The gas flow was controlled by the settings on the container valve and the stopcock on a liquid air cooled condenser-collector at the end of the system. The reactor was made from a 0.5" i.d. nickel tube 18" long and filled with extruded nickel packing. The reaction zone was wrapped with 0.25" copper wire and heated in a Hoskins furnace. The reaction temperatures were noted with a 22-gauge chromel-alumel thermocouple placed at the center of the reaction zone. The temperatures at the surface of the reactor at equilibrium were 2 to 5° higher than those observed inside the unpacked tube.

Conditions.—All experiments were carried out at approximately atmospheric pressure. The average mass flow rates were held between 0.20 and 0.40 g./min. Temperatures were maintained within $\pm 3^\circ$ of the reported values.

Materials.—Trifluoromethyl sulfur pentafluoride: this material was prepared by the electrochemical process.¹ The starting materials were a solution of $(\text{CH}_3)_2\text{S}$, dimethyl sulfide, in anhydrous HF .² The CF_3SF_5 was purified by fractionation and had a b.p. of -20.5° and a molecular weight of not less than 193 and not more than 196.

Perfluoropropylene.—This material was obtained from the Peninsular Chemical Research Co., Gainesville, Fla. It had a molecular weight of 150, b.p. -30° .

Results

Two trials were made to pyrolyze CF_3SF_5 . The first was made at 450°, a flow rate of 0.40 g./min., and an average pressure of 760 mm. No products were recovered that were characterized as different from the starting material. The second trial was made at 500°, a flow rate of 0.20 g./min. and the same pressure as in trial 1. Two grams of C_3F_8 and 2 g. of SF_4 were isolated and identified and some 16 g. of starting material was recovered out of 21 g. of CF_3SF_5 passed through the system. The nickel packing was very slightly attacked during the second trial.

Five trials were made with CF_3SF_5 and C_3F_8 . Generally, the unreacted starting materials were recovered from each trial and reused in the succeeding

trial. The conditions and results of these trials are presented in Table I.

TABLE I

SUMMARY OF REACTIONS OF CF_3SF_5 AND C_3F_8 IN A NICKEL-PACKED REACTOR

| C_3F_8 , g. | CF_3SF_5 , g. | Flow, g./min. | Temp., °C. | Mm. | Products in g. | | | |
|-----------------------------|-------------------------------|---------------|------------|-----|------------------------|---------------|---------------|----------------------|
| | | | | | C_3F_8 | SF_4 | SM^a | b. above -19° |
| 17 | 21 | 0.29 | 425 | 735 | Tr. | Tr. | 37 | 1 |
| 16 | 20 | .32 | 485 | 740 | 1 | 1 | 28 | 4 |
| 26 | 33 | .28 | 512 | 760 | 1 | 13 | 15 | 17 |
| 60 | 75 | .40 | 515 | 760 | 2 | 27 | 70 | 38 |
| 45 | 55 | .28 | 518 | 740 | 1 | 27 | 25 | 47 |
| | | | | | 5 | 68 | | 107 |

^a Starting materials.

The products boiling above -19° were collected and fractionated in appropriate columns. The main fractions isolated and identified were 17 g. C_4F_{10} , 7 g. C_6F_{12} , 15 g. C_6F_{14} and 9 g. C_7F_{16} .

Identification of Products.— C_4F_{10} : This material was recovered from fractionation at between -1° and 1° . It had a molecular weight of between 238 and 240; analysis showed the absence of sulfur.

C_6F_{12} : This material was recovered from fractionation and boiled between 29 and 31° . Its molecular weight was between 286 and 288. It did not show the presence of sulfur. The crude fraction had a melting point range above 10° . Nuclear magnetic resonance spectra were made on aliquots of the sample and from the relative intensity of the CF_2 peaks, it was concluded that the sample contained neo- C_6F_{12} , iso- C_6F_{12} and n- C_6F_{12} , crudely in the ratio 3:2:1.

C_6F_{14} : This material boiled between 57 and 59° . It had a molecular weight of between 338 and 340. It contained no sulfur. The refractive index, n_D^{25} , was 1.2558.

C_7F_{16} : This material boiled between 82 and 83° . It had a molecular weight of 392. It contained no sulfur. The refractive index, n_D^{25} , was 1.2685.

Six grams of product boiled above 83° , and appeared to be fluorocarbon material.

Although the attack on the nickel packing was not too serious even at 518°, one trial, essentially the same as the third trial in the table, was made with the reactor filled with 0.125" NaF pellets. From this trial, 5 g. of C_4F_{10} , 2 g. of C_6F_{12} and 5 g. of C_6F_{14} were isolated and characterized. As only 3 g. of material boiled above 60° , no C_7F_{16} was isolated.

The author is grateful to Dr. F. W. Hoffman and Pvt. N. Muller, and the Army Chemical Center, Edgewood, Md., for the results of the NMR spectra, and to the chemistry Branch of the ONR (Nonr 580(03), NR 356-333) for the sponsorship of this work.

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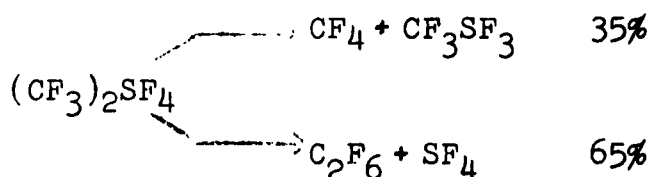
(1) J. H. Simons and co-workers, *J. Electrochem. Soc.*, 95, 47 (1949).
(2) A. F. Clifford, H. K. El-Shamy, H. J. Bmeléus and R. N. Hasseldine, *J. Chem. Soc.*, 2373 (1953).

7.22%). The structure was confirmed by nuclear magnetic resonance spectrum and more recently by an IR comparison spectrum. The yield was 57%.

When $(\text{CF}_3)_2\text{SF}_4$ was pyrolysed at 455°C , 20% by weight was converted to other products mainly CF_4 , C_2F_6 , SF_4 and traces of other materials.

When it was reacted with C_3F_6 olefin at 518°C , traces of CF_4 and quantities of C_2F_6 , C_4F_{10} and C_5F_{12} were isolated. The main product was a mixture of C_5F_{12} isomers from which a purified sample of neo- C_5F_{12} was isolated. It had a M.P. of at least 78.3°C in a closed tube. The yield of C_5F_{12} isomers was better than 50%.

A reaction between $(\text{CF}_3)_2\text{SF}_4$ and $\text{CF}_3\text{N}=\text{CF}_2$ at 520°C failed to produce any $(\text{CF}_3)_2\text{N}-\text{C}_2\text{F}_5$ as all the $\text{CF}_3\text{N}=\text{CF}_2$ was recovered unreacted but the sulfide decomposed as follows:-



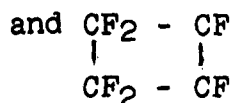
3. Work directed towards finding new ways for activating the reactions of simple fluorocarbons has been started.

A study was conducted with CF_4 to see if this material would react with CO , CO_2 , O_2 , and H_2O both individually and in mixtures. A cupric oxide surface was employed. The reactions were followed in a constant volume vacuum system. The reaction products were passed through water, and the water was tested for fluoride ion. The gases were separated and their molecular weights taken. No reactions were found in the temperature range $200-400^\circ\text{C}$.

The reaction products from the oxidation of CF_3H were studied. The gases were circulated in a constant volume vacuum system. Both copper oxide and silica gel surfaces were employed. The temperature of the surface varied from 320 to 510°C. After reaction, the gases found were CO_2 , H_2O , and where silica was present, SiF_4 . A large amount of white waxy material was also found in the system. This material was found to be a hydrated mixture of silicic and fluorosilicic acids. It was found in large quantities when silica gel was mixed with the catalyst. Silica gel mixed with the copper oxide increased both the rate and completeness of the reaction. These results agreed with the photochemical oxidation reported by Francis and Haszeldine (Jour. Chem. Soc. London, 2151 (1955)).

Mixtures of CF_4 and oxygen, heated over a zinc oxide surface, failed to react in the temperature range 300-496°C. The gases individually were adsorbed by the zinc oxide. Adsorption of oxygen on the surface prevented the subsequent adsorption of CF_4 .

4. Reaction of fluorocarbon olefins with sulfur-perfluoropropylene produces a six-membered heterocyclic ring with the 1,4 dithiane structure in fair yields. This compound is very resistant to attack by aqueous alkali. Other olefins, such as $\text{CF}_2 = \text{CFCl}$



have produced sulfur containing compounds resistant to alkali but in much smaller yields.

Fluorocarbon amidines, $R_fC(NH)NH_2$ have been prepared where R_f is CF_3- , C_2F_5- , or C_3F_7- . Reactions of the amidines to produce the silver and mercury salts have been reported. Condensation reactions of the amidines, wherein ammonia is eliminated have been found to produce the 1,3,5 triazines substituted in the 2,4,6 positions.

A number of N-alkyl substituted fluorocarbon amidines have been prepared by reaction of the fluorocarbon nitriles with organic amines.

The fluorocarbon thioamides $R_fC(S)NH_2$, where R_f is CF_3- , C_2F_5- or C_3F_7- , have been prepared by treating the appropriate fluorocarbon amidine with hydrogen sulfide.

The 2,4,6 substituted 1,3,5 fluorocarbon triazines have been made directly from the fluorocarbon nitriles by thermal polymerization.

REPORTABLE WORK PERFORMED THIS QUARTER

1. Electrochemical Operations on Amino Acid Derivatives

J.A. Young

Improvement of synthetic procedures made possible the accumulation of several hundred grams of $(\text{CH}_3)_2\text{NCH}_2\text{COOCH}_3$ for a run in the small cell. Although the desired $(\text{CF}_3)_2\text{NCF}_2\text{COF}$ was obtained in very good yield based on the percentage of crude product (c. 50%), operating characteristics were poor and consequently the net yield of acid fluoride was small. The ester was, therefore, converted to the amide $(\text{CH}_3)_2\text{NCH}_2\text{CON}(\text{CH}_3)_2$ and another run made. With this compound operating characteristics were better and the following products have been identified; $(\text{CF}_3)_2\text{NCOF}$, $(\text{CF}_3)_3\text{N}$, and $(\text{CF}_3)_2\text{NCF}_2\text{COF}$.

The methyl ester and the amide of $(\text{CF}_3)_2\text{NCF}_2\text{COOH}$ have been made, and both dissolve in aq. NaOH without generation of fluoride ion. This indicates that the acid and its derivatives will be stable, in contrast to $(\text{CF}_3)_2\text{NCOOH}$, and consequently will be of greater synthetic value.

Identification of Compounds Previously Only Tentatively Identified

Elemental analyses and NMR spectra have confirmed the formulas previously suggested for $\text{O}(\text{CF}_2\text{CF}_2)_2\text{NCOF}$ and $\text{CF}_3\text{CON}(\text{CF}_3)_2$. Positive identification of the former shows that it is possible to produce rather complex fluorocarbon derivatives by the electrochemical method, though the yields, with the present knowledge of the process, can be expected to be low.

$\text{CF}_3\text{CON}(\text{CF}_3)_2$ is the first perfluoro amide to be reported. Preliminary investigation indicates that its chemistry is not identical with that of amides containing hydrogen.

Pyrolysis of $\text{CF}_2\text{OCF}_2\text{CF}_2\text{NC}_2\text{F}_5$

To secure sufficient amounts of cracked products for study of this reaction, it was necessary to go to a temperature of nearly 700°C . On the basis of present data, the most likely steps in the pyrolysis seem to be ring cleavage, loss of COF_2 , and rearrangement of the resulting fragments into thermally stable molecules containing the carbon-nitrogen double bond. There may be alternative reaction paths, as some of the products do not completely agree with this proposal. One peculiarity is the presence of a material which appears in the fraction boiling in the range from -20 to -13° , but melts above room temperature under autogenous pressure, in a more purified state.

2. The Electrochemical Preparation of C_2F_5SF and $(C_2F_5)_2SF_4$

These materials were prepared by passing a D.C. current through a solution of dimethyl sulphide in anhydrous HF. The electrochemical process was performed in an electrochemical cell of nominally 20 amperes capacity. The initial concentration of .005 mole ratio dimethyl sulfide to HF permitted a current of 17 amperes at 4.8 volts. D.C. Two hundred and seventy grams of $(CH_3)_2S$ was used in the process and this yielded some 355 grams of fluorine containing products trapable in a dry-ice cooled trap. From the resulting product some 200 grams of $C_2F_5SF_5$, BP $11.3^\circ C$ (S $12.70 \pm 0.10\%$, F $77.3 \pm 0.4\%$ - theoretical 13% and 77.3% resp.) and 26 grams $(C_2F_5)_2SF_4$ B.P. 68.0° (S $9.22 \pm .12\%$, F $76.1 \pm 0.3\%$, - theoretical 9.25% and 76.9% resp.). $(CF_3)_2SF_4$ and $C_4F_9SF_5$ boil at 17.4° and 70° , respectively.

The S and F analysis were performed somewhat similarly to the method of Cady and Silvey (J.A.C.S. 72 3624 (1950)) with the exceptions that the fusions were performed in a sealed glass tube at $640^\circ C$. and $S^{=}$ was removed by precipitation with a known quantity of standard silver nitrate solution before F^- analysis were performed.

IR spectra were made on both compounds and the data is offered in the following table:-

IR Spectra of $C_2F_5SF_5$ and $(C_2F_5)_2SF_4$

| $C_2F_5SF_5$ | | $(C_2F_5)_2SF_4$ | |
|----------------|---------------------------|------------------|---------------------------|
| <u>Microns</u> | <u>% Absorb. Relative</u> | <u>Microns</u> | <u>% Absorb. Relative</u> |
| 6.27 | 5 | | |
| 6.60 | 5 | 6.88 | 5 |
| 7.48 | 60 | 7.50 | 40 |
| 7.97 | 94 | 7.96 | 90 |
| 8.12 | 94 | 8.15 | 87 |
| 8.64 | 89 | 8.67 | 70 |
| 9.92 | 27 | 10.01 | 77 |
| 11.10 | 97 | 11.10 | 12 |
| 11.63 | 99 | 11.71 | 88 |
| 13.33 | 68 | 12.77 | 36 |
| 14.47 | 28 | 13.31 | 5 |
| | | 13.87 | 3 |
| | | 14.35 | 79 |

The Reaction of CF_3SF_5 and C_3F_6 Olefin Under Moderate Pressures

CF_3SF_5 (.11 mole) and C_3F_6 (.17 mole) were condensed in a stainless steel cylinder (tested at 500°C and 1000 psi with N_2) closed with a 2000 psi Monel valve and having a gauge for pressure attached. This was heated in a tube furnace with a thermocouple well attached to the inner wall. The clearance was less than 1/16". The temperature was raised at the rate of less than 1°C. per minute.

The initially observed pressure at room temperature was 75 psi. As the temperature rose, the pressure increased until a condition of 370 psi at 426°C was noted. The pressure dropped slowly to 320 psi and did not rise again until the temperature had risen to 480°.

Examination of the products showed a small residue of starting material, the usual theoretical quantity of base unstable sulphur fluorides, and the following quantities of (isomeric) fluorocarbon homologues C₄F₁₀, 1.0 grams; C₅F₁₂ (some neo isomer in evidence) 7.0 grams; C₇F₁₆, 7.0 grams; C₇F₁₆, 4.0 grams and residues with a molecular weight up to 404, 2.0 grams.

The products are observed to be the same as those obtained when the starting materials are passed through a furnace at 520°C in equimolar quantities at one atmosphere but the conversions are higher, occur at a lower temperature and the product distribution is modified as noted in the following table:-

Normalized % Yield Fluorocarbons

| <u>Compound</u> | <u>Dynamic (512°C)</u> | <u>Static (430°C)</u> |
|--------------------------------|------------------------|-----------------------|
| C ₄ F ₁₀ | 35 | 8 |
| C ₅ F ₁₂ | 15 | 36 |
| C ₆ F ₁₄ | 31 | 36 |
| C ₇ F ₁₆ | 19 | 20 |

Pyrolysis of C₂F₅SF₅

Fifteen grams C₂F₅SF₅ (B.P. 11,3°C) were passed through a furnace at 500°C at an average rate of 0.15 g/min. at about one

atmosphere pressure. About 7.0 grams of sulphur fluorides were obtained, slightly more than trace amounts being identified as SF_6 (base insoluble, subliming M.W. 148-150). When the residual 8 grams was distilled, 3 grams was found to be C_2F_6 and 5 grams was C_4F_{10} while no starting material was recovered. From previous work it is noted that CF_3SF_5 will pyrolyze only 20% and $(\text{CF}_3)_2\text{SF}_4$ 40% under essentially the same conditions. It seemed that $\text{C}_2\text{F}_5\text{SF}_5$ should react with C_3F_6 at essentially lower temperatures.

The Reaction of $\text{C}_2\text{F}_5\text{SF}_5$ with C_3F_6 Under Moderate Pressure

Using the same pressure equipment described above, 0.18 mole C_3F_6 and 0.085 mole $\text{C}_2\text{F}_5\text{SF}_5$ were reacted. The reaction began at 390° and 325 psi. When the reaction products were fractionated 8.5 gram sulphur fluorides were isolated of which 1.0 grams was SF_6 . Of the fluorocarbons isolated boiling above room temperature, 3.5 g. was C_5F_{12} (no neo isomer), 6.0 grams C_6F_{14} , 6.0 g. C_7F_{16} , 5.0 g. C_8F_{18} and 3.0 g. pot residue which failed to show the presence of sulphur on analysis and had a molecular weight up to 544 ± 25 .

J.A. Wethington, Jr.

3. Preliminary work has been done on the reactions of fluoro-carbons and other fluorine-containing compounds with alkali metal vapors. The reaction of SF_6 with sodium was found to be so exothermic that the pyrex reactor was melted. By using potassium and protecting the glass with a nickel sleeve, potassium could be reacted with SF_6 . No interesting products were obtained. SF_6 and CF_4 mixtures have been reacted with potassium vapor. The reaction could be controlled without difficulty. The products found were carbon, potassium fluoride and potassium sulfide.

H. C. Brown

4. Perfluoroalkyl diamidines.- Considerable difficulty has been encountered in producing perfluoroglutaronitrile from the corresponding diamide in yields sufficient for carrying out the proposed reaction with ammonia to make the perfluoro diamidine. Dehydration of the diamide with phosphorus pentoxide results in extensive decomposition with very little production of dinitrile.

Reaction of C_7F_{14} with Sulfur.- In previous reports, the reaction of perfluoropropene, $CF_3CF=CF_2$, with sulfur to produce a perfluorodithiane has been described. In this reaction the carbon atoms connected by the double bond take part in the formation of the ring and therefore a $-CF_3$ substituted dithiane results. It seemed possible that if a longer chain were attached to the terminal olefinic portion of the molecule, ring formation might be hindered and a linear polymer formed. Therefore, a compound reported to have the formula $CF_3(CF_2)_4CF=CF_2$ was made by pyrolysis of the sodium salt of perfluorooctanoic acid.

In each of the experiments performed with this C_7 olefin, 26.6 (0.076 moles) of the olefin was sealed in an evacuated heavy wall Pyrex glass tube containing 0.1 mole of sulfur. The first run was made at $280-300^\circ$ for 15 hours. No reaction was apparent and the starting material was recovered. A second run at a higher temperature resulted in explosion of the tube. A third run at 350° for 16 hours was made and the total reaction product refluxed with 10% sodium hydroxide solution. This treatment left only about 1 ml. of

yellow liquid stable to hydrolysis, even though a large part of the reaction mixture appeared to be unreacted olefin. A fourth run at 385° resulted in a violent explosion before the temperature reached the preset value. A fifth run at 350° for 36 hours produced much carbon and hydrolyzable sulfur fluorides. Little carbon disulfide was found although it is quite frequently produced in pyrolytic reactions of fluorocarbon olefins with sulfur.

From this work it appears that a rapid reaction of the olefin with sulfur takes place above 350° and possibly a different reaction when the temperature is held at 350° or lower. The unexpected behavior may be due to a variation reported terminal unsaturation.

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